

COMPARISON OF THE ELECTRONIC STRUCTURES AND ENERGETICS OF FERROELECTRIC LiNbO_3 and LiTaO_3

IRIS INBAR

R.E. COHEN

Carnegie Institution of Washington, Geophysical Laboratory,

5251 Broad Branch Rd, N.W. Washington, D.C. 20015

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Abstract

Extensive LAPW frozen phonon calculations were performed in order to understand the origin of ferroelectricity in LiTaO_3 and LiNbO_3 . Displacement of the Li atoms alone results in an anharmonic single well, whereas displacements of oxygen and lithium together result in deep double wells, much deeper than the transition temperatures, T_C . This is contrary to current theories which model the underlying potential as a triple well potential for the lithium atoms. Our results support an order-disorder model for the oxygen atoms as the driving mechanism for the ferroelectric instability. Oxygen displacements alone against the transition metal atoms result in shallower double wells as a result of oxygen-lithium overlap so that the lithium and oxygen displacements are strongly coupled. We find large hybridization between the oxygens and the transition metal atoms. Thus ferroelectricity in the $\text{Li}(\text{Nb,Ta})\text{O}_3$ system is similar in origin to ferroelectricity in the perovskites. We also find that the electronic structures of LiTaO_3 and LiNbO_3 are very similar and hardly

change during the phase transition.

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I. INTRODUCTION

The origin of ferroelectricity in the two well known ferroelectric systems, LiNbO_3 and LiTaO_3 , has been subject to intense study since the discovery of LiNbO_3 in 1949¹. They have many applications in optical, electro-optical and piezoelectric devices, but the fundamental physics that leads to their ferroelectric behavior have not been studied. Their transition temperatures, which are among the highest known ferroelectric transition temperatures, are quite different, 1480 K for LiNbO_3 and 950 K for LiTaO_3 . The electronic origin of their different T_C is a mystery since Nb^{5+} and Ta^{5+} behave very similarly, and structurally these materials are almost identical. The origin of their ferroelectric instability as well as their different transition temperatures is investigated.

Both materials undergo only one structural phase transition. The paraelectric structure has a 10 atom unit cell and the average structure belongs to the $R\bar{3}c$ space group, The atomic arrangement consists of oxygen octahedra sharing faces along the polar trigonal axis. The transition metal atoms occupy the centers of oxygen octahedra, and the average Li atom position lies on the face between two adjacent oxygen octahedra (Fig. 1a). The ferroelectric structure is rhombohedral, and belongs to the space group $R3c$. The transition metal atom is displaced from the center of the oxygen octahedra along the trigonal axis. The next oxygen octahedron along this axis is empty and the adjacent octahedron has a Li atom ferroelectrically displaced from the oxygen face in the spontaneous polarization P_s direction (Fig. 1b). Glass in 1968 and later Johnston *et al.* have determined, using dielectric and thermal measurements, that the phase transformation in these systems is continuous^{2,3}.

Whether the transition is displacive or order-disorder has been much discussed and confusion abounds. A displacive phase transition is one where the local potential in the mean field of the rest of the crystal has a single minima, and is characterized by a temperature dependent optic mode approaching zero as the temperature reaches T_C . Temperature dependence measurements of Raman, Rayleigh scattering³ and infrared reflectivity⁴⁻⁶ show soft mode behavior for one polar A_1 (TO) optic mode in the ferroelectric phase. This soft

mode crosses many E modes (whose eigenvectors give ionic displacements perpendicular to the polar axis) , and thus this specific mode is difficult to trace in detail. Tomeno and Matsumura⁷ measured the dielectric constants of LiTaO₃ and found a large Curie constant, and interpreted their results as indicative of a displacive transition.

Evidence for the transition having an order-disorder character came from Penna *et al.*⁸⁻¹¹, who observed no mode softening for LiTaO₃ for the A₁ (TO) mode, followed by Chowdhury *et al.*¹² who performed neutron scattering experiments on LiNbO₃, and also failed to observe any softening of the A₁ mode. Okamoto *et al.*¹³ used Raman scattering to study LiNbO₃ between room temperature and 1225K and saw two of the three A₁ modes (which are, at room temperature, TO, LO and TO at 250, 270 and 274 cm⁻¹, respectively), and observed anomalous behavior for one of them (at 274 cm⁻¹) as the temperature reached T_c. They noted that the decrease in the peak frequency was mostly due to the rapid increase in damping as the linewidth had a divergent form in temperature, whereas the quasiharmonic frequency remained almost temperature-independent. Their conclusion was therefore that LiNbO₃ does not exhibit a typical displacive transition, but rather resembles an order-disorder system. Zhang *et al.*¹⁴ reported these measurements on LiTaO₃, and found the same kind of behavior. In an order-disorder phase transition the local potential is characterized by a double (or more) well, with the thermal energy kT_C much smaller than the well depth and no soft phonon mode exist since phonons now oscillate within each well and the wells remain essentially unchanged throughout the phase transition. These transitions are characterized by a diffusive soft mode which is not a phonon but represent large amplitude thermal hopping between the wells. At T above T_C the crystal is non-polar in a thermally averaged sense.

Jayaraman *et al.*¹⁵ argued for an order-disorder type transition because they saw little pressure dependence of the Raman mode; they also emphasize the difference from ferroelectric perovskites, which show a strong pressure dependence. Raptis¹⁶ measured and analyzed Raman modes of LiTaO₃ between room temperature and 1200K and observed softening of this A₁ mode (along with others) to a certain degree. However, the decrease was characterized with an order-disorder model. Catchen *et al.*¹⁷ used perturbed-angular-correlation

(PAC) spectroscopy to measure nuclei-electric-quadrupole interactions at the Li sites over a temperature range of 295-1100K, and Cheng *et al.* ^{f18} studied inelastic neutron scattering from room temperature up to 800⁰C (1100 K) in LiTaO₃; both failed to observe mode softening, therefore not supporting the displacive picture for the phase transition. Tezuka *et al.*¹⁹ used hyper-Raman and Raman spectra of LiTaO₃ between 14 and 1200 K. No evidence was found for the softening of the A_1 mode; however, a strong Debye-type relaxational mode was found in the two phases, suggesting an order-disorder type transition. They interpreted the anomalous line shape of an A_1 mode in terms of coupling with relaxational modes.

Most ferroelectric systems are thought of as exhibiting displacive behavior far from the transition temperature region and order-disorder characteristics near T_C . In the Li(Nb,Ta)O₃ systems this conclusion is supported by a number of studies^{20–22}.

In other ferroelectric oxides, like the perovskites KTaO₃ and KNbO₃, the mechanism behind the phase transition has also been debated. Evidence for the transition being of the displacive type are presented by Nunes *et al.*²³ and Samara²⁴, while Comes *et al.*²⁵ and PAC experiments by Dougherty *et al.*²⁶ point to it being of the order-disorder type. Sokoloff *et al.*²⁷ have studied Raman scattering of KNbO₃ and BaTiO₃ and discovered central peaks which have line shapes and thermal dependence characteristics of Debye relaxation modes as well as symmetry properties consistent with the eight-site model. A theoretical study by Edwardson of KNbO₃²⁸, using interacting polarizable ions in static and dynamic simulations found a mixture of order-disorder and displacive type behavior. Postnikov *et al.*^{29,30} carried out an LMTO study examining the total energy of KNbO₃ in the tetragonal and rhombohedral phases. These calculations found that displacing the Nb atom along the $\langle 100 \rangle$ direction from its tetragonal cell position corresponds to a saddle point on the total energy surface. This becomes a minima when the lattice strain is included. They have also carried out total energy calculations for KTaO₃ which found no ferroelectric instability for the calculated volume. They were able to induce a phase transition by applying negative pressure (expanding the lattice). An XAFS study of KTN by Hanske-Petitpierre *et al.*³¹ found that the ferroelectric transition is not displacive and involves orientational order-disorder transi-

tion of the Nb atom. A recent first principles investigation of eight perovskites^{32,33} suggests that in materials like KNbO_3 and BaTiO_3 , which are rhombohedral at $T=0$, the sequence of successive transitions is explained via the eight site model, where the order parameter in the paraelectric phase fluctuates between the eight minima in the $[111]$ directions. These sites are minima at the cubic phase, before the development of the strain.

The theories developed thus far for the LiTaO_3 and LiNbO_3 systems usually are based on the Lines model³⁴. M. E. Lines applied his effective-field theory to LiTaO_3 , and parametrized it as a displacive ferroelectric due to the data available at the time by Johnston and Kaminow³, and assumed a triple well potential for the Li atoms. Abrahams *et al.*³⁵ performed neutron scattering of LiTaO_3 between room temperature and 940 K, and discovered that, above T_C , the lithium atom positions in LiTaO_3 become disordered and hop among the centrosymmetric position and sites at $\pm 0.37 \text{ \AA}$ along the optic axis. Similar measurements for LiNbO_3 show the same kind of behavior³⁶. The neutron scattering data is the cornerstone behind all theories modeling this ferroelectric transition as an order-disorder mechanism with the Li ions hopping among the centrosymmetric sites and the adjacent octahedral sites. This approach was adopted by Birnie^{37–39}, who modeled the Li hopping as a Frenkel defect, and later by Bakker *et al.*⁴⁰, who used this data in addition to the triple well Lines model as a basis for a quantum-mechanical description of the phase transformation in LiTaO_3 . Bakker *et al.* predicted and observed⁴¹ a 32 cm^{-1} excitation which they ascribed to Li motions between the central and lowest wells. This excitation frequency has not been observed in other studies, however⁴².

II. METHOD

The Kohn-Sham equations^{43,44} are solved self-consistently using the full potential Linearized Augmented Plane Wave (LAPW) method⁴⁵, where the electronic many-body exchange-correlation interactions are described by the local density approximation (LDA) using Hedin-Lundqvist parametrization⁴⁶. There are no shape approximations for the charge

density or the potential. This method has proved predictive in many previous studies. Examples include the prediction of a high pressure phase transformation in silica⁴⁷, studies of iron at high pressures^{48,49} studies of Al_2O_3 ⁵⁰, MgO and CaO ⁵¹, MgSiO_3 ⁵² and high temperature superconductors⁵³. This method was previously applied successfully to perovskite ferroelectrics like BaTiO_3 , PbTiO_3 ⁵⁴ and KNbO_3 ⁵⁵.

We use the LAPW+LO method⁵⁶ which uses a mixed basis consisting of the LAPW basis plus extra localized orbitals inside the muffin tin spheres. The extra local orbitals remove a Li s ghost state and relax the valence states. It also allows the use of a single energy window. Local orbitals included s for Li, s and p for O and s , p and d for the Nb and Ta atoms. Other details of the calculations include a muffin tin size of 1.6 Bohr for the Li and 2.0 Bohr for the Nb and Ta atoms. The oxygen's muffin tin radius was 1.6 Bohr for oxygen-Nb separation up to 1.882Å (3.556 Bohr). The corresponding distance in LiTaO_3 is O-Ta up to 1.8845Å (3.562 Bohr). At this point the oxygen muffin tin radius was decreased to 1.552 Bohr. For smaller separations the muffin tin radius was 1.506 Bohr. In order to be able to compare the energies calculated using different muffin tin radii, we have repeated calculations with the three sets of muffin tin radii to find the energy shift due to this change in the muffin tin radii, and have assumed that this small shift (~ 7 mRy) is constant for small displacements of atoms.

A 4x4x4 special k-point mesh was used which generates a total of 10 k-points in the irreducible zone. To test energy convergence, the energies at the symmetric and experimental structures of both LiTaO_3 and LiNbO_3 were also calculated with a 6x6x6 mesh which generates 28 k-points in the irreducible zone, and these energies are shown in Table I. The change in energy difference for the two k-point sets between the experimental and the symmetric configurations is 0.069 mRy for LiNbO_3 and 0.3 mRy for LiTaO_3 , demonstrating convergence.

The RK_{max} parameter was set to 7.0 which gives approximately 1150 basis functions for the LiTaO_3 calculations and 1050 functions for LiNbO_3 . The core states were calculated fully relativistically and the valence states semi-relativistically. For each Ta atom, the states

up to 4f were included in the core, and as a result 0.588 electrons extended beyond the muffin tin sphere. For each Nb atom states up to 4s were included in the core and only 0.07 core electrons extended beyond the sphere; core electrons that spill out of the muffin tins see an extrapolated spherical core potential. Also, in LiNbO_3 the Li atom s states were included as bands, whereas in LiTaO_3 they were treated as core states.

III. RESULTS AND DISCUSSION

A. Energetics

We have calculated the potential energy surfaces along the experimental soft mode coordinate. To test the sensitivity to the different lattice parameters, the total energy of LiNbO_3 was calculated in the ferroelectric configuration using both the LiNbO_3 lattice parameters ($a_H=5.14829\text{\AA}$ and $c_H=13.8631\text{\AA}$)⁵⁷, and the LiTaO_3 lattice parameters ($a_H=5.15428\text{\AA}$ and $c_H=13.78351\text{\AA}$)³⁵, a difference of 0.75% in the c/a ratio. The effect of this strain on the total energies was almost negligible; slightly less than 1 mRy or 5.5% of the well depth. This is in contrast to the case of the perovskites; e.g. PbTiO_3 , where a strong dependence of the total energy on the tetragonal strain was observed, and the energy decreases markedly, about 35% of the well depth for the experimental 6% c/a strain⁵⁴. Also the total energy of LiNbO_3 using both the experimental LiNbO_3 atomic positions (Li at (0.2829,0.2829,0.2829), Nb at (0,0,0) and Oxygen at (0.1139,0.3601,-0.2799))⁵⁷ and the LiTaO_3 atomic positions (Li at (0.279,0.279,0.279), Ta at (0,0,0) and Oxygen at (0.1188,0.3622,-0.2749))³⁵ were calculated. The resulting wells are less than 1 mRy different, the LiNbO_3 atomic positions yielding the deeper well. For the purpose of comparison, except for a few more points which yielded the same results (energy differences of less than 1 mRy), all points were calculated using the experimental lattice parameters and positions of LiTaO_3 to facilitate comparison of the effects of chemistry on ferroelectric behavior and electronic structure. Table I summarizes the results for LiTaO_3 and LiNbO_3 . The first column refers to the displaced atoms, and to

the amount of displacement as a fraction of the paraelectric to experimental ferroelectric normal mode amplitude. Note that one distortion of LiTaO_3 published earlier⁵⁸ was not along the soft mode coordinate; the present results correct this error.

Figure 2a shows the potential energy surfaces of LiTaO_3 with respect to displacements of Li only (upper curves), oxygen only (middle, shallow double wells) and Li+O (lower curves). Figure 2b shows the same picture for LiNbO_3 . The lithium displacements along the soft mode coordinate result in a single anharmonic well with low curvature. Displacing only the oxygens against the transition metal atoms results in shallow double wells, and the deep double wells are the result of the Li+O displacements along the experimental ferroelectric coordinate.

The wells resulting from the oxygen and lithium displacements have well depths of 17.3 mRy (2739 K) and 18.3 mRy (2858 K) for LiTaO_3 and LiNbO_3 , respectively. Both wells are much deeper than the experimental transition temperatures, which is consistent with an order-disorder character for the phase transition.

The energy was fit to a fourth order polynomial in normal mode amplitude, $Q = \sqrt{\sum_i m_i u_i^2}$. The Schrödinger equation was solved numerically to obtain the eigenstates assuming one-dimensional non-interacting anharmonic oscillators along the soft-mode coordinate. Figure 3 shows the energy surface as a function of the normal mode amplitude, Q , and the energy levels. We can see that the two wells have a different shape due to the factor of about two in mass of Nb and Ta, and thus the Nb approximately displaces twice as much as the Ta relative to the center of mass, which results in a different normal mode amplitude Q . The energy difference between the ground and lowest excited state gives a frequency for LiTaO_3 of 270 cm^{-1} in fairly good agreement with the experimental Raman frequency of $201\text{-}225 \text{ cm}^{-1}$ considering the one dimensional noninteracting oscillators approximation. For LiNbO_3 , the calculated frequency is 250 cm^{-1} , in excellent agreement with experimental data of about $250\text{-}275 \text{ cm}^{-1}$.

These results indicate that these structural phase transitions are *not* dominated energetically by the displacements of the lithium alone. The potential energy surfaces show that

the deep double wells are the result of the *coupled* motion of lithiums and oxygens. Displacement of the lithiums alone hardly changes the energy of the system. This is in contrast to current theories which model the displacement of the lithiums as the driving mechanism for the ferroelectric instability.

In order to understand the oxygen-lithium coupling, we calculated the dynamical matrices for the LAPW and Madelung energies (assuming fully charged ions) for both materials. The LAPW and Madelung energies were fitted to a 4th order polynomial surfaces in the normal mode coordinates of the lithium and oxygen (Q_{Li} and Q_O). The second derivatives of these energy surfaces at zero displacements are the coefficients of the dynamical matrices. Table III shows the coefficients of the fit for the total energy of $LiNbO_3$ and $LiTaO_3$; all the coefficients for $LiNbO_3$ and $LiTaO_3$ are well constrained except the coefficient of Q_{Li}^2 , which means the potential surface describing the displacement of the lithium only could be either a single anharmonic well or a very shallow double well (corresponding to a positive or a negative sign). Linear and cubic terms (e.g; Q and Q^3) are excluded from the fit based on symmetry considerations, and terms which are not along the coordinates calculated; Q_{Li} , Q_O and $Q_{Li,O}$, are excluded from the fit since they degrade the variances of the quadratic coefficient. These include terms like $Q_{Li}^3 Q_O$ and $Q_O^3 Q_{Li}$. The dynamical matrix in units of $Ryd^2 \text{\AA}^{-2} amu$ representing the LAPW energies of $LiNbO_3$ and $LiTaO_3$ are

$$D_{LAPW}(LiNbO_3) = \begin{pmatrix} D_{Li} & D_{Li,O} \\ D_{Li,O} & D_O \end{pmatrix} = \begin{pmatrix} -0.001 & -0.012 \\ -0.012 & -0.015 \end{pmatrix}$$

$$D_{LAPW}(LiTaO_3) = \begin{pmatrix} 0.0018 & -0.012 \\ -0.012 & -0.023 \end{pmatrix}.$$

The lithium-only contributions (D_{Li}) are the smallest (an order of magnitude smaller than the rest), the oxygens only contributions are larger, with D_O in $LiTaO_3$ larger than $LiNbO_3$.

Whether the origin of lithium and oxygen coupling is Coulombic can be determined by looking at the Madelung contribution to the dynamical matrices. The Madelung energies were calculated using experimental positions and lattice parameters and full ionic charges.

The second derivatives at zero displacements, which are the elements in the dynamical matrix, were calculated numerically and are shown in Table III. In the case of LiNbO_3 and LiTaO_3 the Madelung contributions to the dynamical matrix are

$$D_{MAD}(\text{LiNbO}_3) = \begin{pmatrix} 0.038 & 0.004 \\ 0.004 & -0.171 \end{pmatrix}$$

$$D_{MAD}(\text{LiTaO}_3) = \begin{pmatrix} 0.04 & 0.003 \\ 0.003 & -0.162 \end{pmatrix}.$$

As expected, D_O has the largest magnitude, followed by D_{Li} . The coupling term between the lithiums and the oxygens is in fact zero. This means that the origin of the lithium-oxygen coupling is *not* pure Coulombic (Madelung).

Another possibility is the polarization of the oxygens by the lithium displacement, leading to changes in Nb(Ta)-O bonding. The experimental ferroelectric configuration generates an effective dipole at the lithium sites. This dipole field can polarize the oxygens and drive them off center, yielding a ferroelectric distortion. We have plotted the self-consistent charge densities in two configurations; in one only the oxygens are displaced and in the other both the oxygens and the lithiums are displaced. In order to see the effects of displacing the lithiums we subtracted the two charge densities. This is shown in Fig. 5 where the charge density contours are plotted on a scale of -0.1 to 0.1 electrons/bohr³ and the contour interval is 0.002 electrons/bohr³. A large dipole is seen at the lithium sites due to the displacement of the lithiums. Little polarization of the oxygens is observed; there is no evidence for any large dynamical covalency effects. We can therefore eliminate the possibility of oxygen-lithium coupling through either Madelung or polarization effects.

Another possible source for the oxygen-lithium coupling is through the crystal structure. It is important to notice that the oxygens move not only along the c axis, but rather have sizable displacements along the a and b axes as well. We have tested the importance of these displacements by moving only the oxygens along the c component of the experimental ferroelectric displacement (the polar axis). The resulting energy curve was far shallower than

the energy surface which resulted from moving the oxygens only along the experimental soft mode coordinate. This is shown in Fig. 4 where the upper curve represents the displacements of the oxygens along the polar axis only and the lower, deeper well represents the total energy when displacing the oxygens along the experimental ferroelectric distortion (along a,b and c axes). The reason for these big energy differences can be seen from Table II which shows the Ta-O, Nb-O and Li-O bond lengths. The ionic radii of Li is about 0.6 \AA , that of Ta or Nb is about 0.6 \AA and the ionic radii of oxygen is about 1.4 \AA ⁵⁹, making the sum of each pair (Li-O, Nb-O and Ta-O) about 2.0 \AA . When the oxygens are displaced only along the c axis, the oxygen-Nb (Ta) separation becomes only $1.83 (1.86) \text{ \AA}$ which is about $0.17 (0.14) \text{ \AA}$ shorter than the sum of the ionic radii (about 8 (7)%). Therefore it is energetically favorable for the oxygens to displace in the a-b plane as they move along the c axis.

If we now consider the experimental ferroelectric displacement of only the oxygens and the experimental ferroelectric *coupled* displacement of the oxygens and lithiums, displacing the oxygens only results in a Li-O separation which is also shorter than the sum of their ionic radii (Table II). This explains why the wells associated with the oxygen displacements alone are shallower than those obtained with the displacement of *both* the lithiums and oxygens. The origin of the Li-O coupling is therefore the fact that motion of the oxygens alone yields a Li-O distance that is larger than the sum of their ionic radii, resulting in a deeper well for the coupled motion (in which the Li and oxygens move away from each other).

We can therefore conclude that the driving mechanism behind the phase transformation in these systems is the displacement of the oxygens towards the transition metal atoms. Displacement of the oxygens in the direction of the transition metal atoms only (the c axis) would result in too short Nb (Ta)-oxygen bonds. The oxygens therefore move also in the plane perpendicular to the c axis, towards the lithiums. This shortens the lithium-oxygen bond so that the lithium displacements are coupled with the oxygen motions.

The transition temperature, T_C , cannot be calculated directly from the zone center energetics. In the usual models for ferroelectric phase transitions, T_C is related to the relative strength of the local (on-site) and coupling terms in the energy⁶⁰. Since we find the zone

center energetics to be similar, the difference in T_C must be due to differences in the energetics at the zone boundary.

In order to understand the origin of the ferroelectric distortion, we next examine the electronic structure of these materials.

B. Electronic Structure

One goal of this research is to understand the origin of ferroelectricity in LiTaO_3 and LiNbO_3 and the difference in T_C from their electronic structure. Fig. 6a compares the electronic density of states for LiTaO_3 and LiNbO_3 , both at the ferroelectric configuration. The energy scales are lined up with the top of the valence bands at zero energy. It is clear that the total density of states of these two materials is very similar. We can look further at the different contributions to the density of states; Fig. 6b compares the partial density of the Ta 5d state and the Nb 4d state both in the ferroelectric phase. The top of the valence band is composed mostly of oxygen p states. This figure shows a large density of transition metal d states in the valence band which means that the oxygen p states in these two materials are hybridized with the d states. The Nb d states have a large peak at the bottom of this band which is missing in the case of the 5d states of the Ta atom. The origin of this peak is the fact that the lowest valence bands of LiNbO_3 (the bands at about -4.5 eV or -0.35 Ryd) are less dispersive than the lowest valence bands of LiTaO_3 . This will be further discussed later. The same conclusion is derived from Fig. 6c of the partial density of the oxygen p state of the two materials in the valence band in the ferroelectric structure. Here too, the densities of states are very similar. The same peak at the bottom of the band is seen here for the LiNbO_3 , which is missing in the valence band of LiTaO_3 . All three figures that compare the total and partial density of states of the two materials in their ferroelectric phase show large hybridization between the transition metal d states and the oxygen p states, which is the reason for the oxygen displacements towards the transition metal atoms.

Next we compare the densities of states in the paraelectric and the ferroelectric phases. Fig. 7a illustrates the total density of states of LiNbO_3 in the paraelectric (solid line) and the ferroelectric (dashed line) phases. The bands in the two phases look similar except that the bands at the ferroelectric phase are slightly wider than the bands at the paraelectric phase. Fig. 7b compares the Nb 4d state both in the paraelectric (solid line) and the ferroelectric (dashed line) phases and Fig. 7c shows the Ta 5d states in the two configurations. The large peak at the lower part of this band (the peak at about -0.35 Ryd or -4.5 eV) is shifted in the ferroelectric case to higher energies. Fig. 7d shows the density of oxygen p states of LiNbO_3 at the two phases. The peak at the bottom of the band is shifted in the ferroelectric phase from the paraelectric one. These figures indicate that the electronic structure at the paraelectric and the ferroelectric phases are quite similar. Fig. 7e compares the lithium 2s character in the paraelectric and ferroelectric phases. It is evident that the lithium is almost completely ionized and that its electronic distribution does not change during the phase transition.

Fig. 8 shows the band structure of LiNbO_3 in the ferroelectric state. The band gap is indirect, the top of the valence band is between Γ and Z, and the bottom of the conduction band is at the Γ point. The Brillouin zone for the rhombohedral lattice⁶¹ is illustrated in the inset in the figure. The energy between the Z and the A point was calculated along a straight line between the two points not along the Brillouin zone face for the purpose of comparison with Ching *et al.*'s results⁶².

The band gap is 3.1 eV which is about 15 % lower than the value obtained from optical measurements of the near stoichiometric sample^{63,64} of 3.78 eV. The lithium 2s states are separated by 13.6 eV from the oxygen 2s states. These bands would not appear in the LiTaO_3 band structure since the lithium 2s states were treated as core states; these bands are very flat. The oxygen 2s are separated by 10 eV from the valence bands. The lowest conduction bands are the Nb 4d states for LiNbO_3 or Ta 5d states for LiTaO_3 . We have also compared this band structure with Ching *et al.*⁶² who used the OLCAO method and got a band gap of 3.56 eV and the bands compare well with our results.

Fig. 9a and b show the band structure for LiTaO_3 and LiNbO_3 , respectively. Each figure shows the ferroelectric (solid line) and the paraelectric (dashed line) phases. The changes observed between the ferroelectric and paraelectric bands are the band gap which is larger in the ferroelectric phase by about 15 % and the band width, especially the conduction band, which is larger in the paraelectric phase.

The band structures of LiTaO_3 (dashed line) and LiNbO_3 (solid line) both in the ferroelectric phase, are shown in Fig. 10. The only difference between these two band structures is the larger band gap, by about 1 eV (30 %), in LiTaO_3 . The conduction bands are shifted by 1 eV from each other, but otherwise, their structure is almost the same. The valence bands are almost identical, which is consistent with the results of the total energy calculations where the two well depths were found to be very close to each other (within 1.2 mRy of each other) and the fact that the number of valence electrons in the muffin tins in both materials was similar. The only difference which was found between the two electronic structures was in the size of the band gap and the less dispersive nature of one band. The difference in the band gap will have an effect on quantities which include summing over unoccupied states as well as the occupied ones, like the polarizability. This difference will lead to different phonon dispersion in the two materials, and thus to different T_C 's. Zone boundary or linear response calculations are necessary to further explore this issue.

C. Comparison to the Perovskites

Previously we studied the difference between the self-consistent charge densities and charge densities computed using overlapping ions with the PIB model for both LiTaO_3 and LiNbO_3 in the ferroelectric phase⁶⁵. In the PIB model which is a non-empirical ionic model⁶⁶, the charge densities are calculated via a Gordon-Kim type model⁶⁷, where the ions are allowed to breath corresponding to changes in the crystal potentials. The comparison indicated large hybridizations between the Ta atoms and the oxygens and between the Nb atoms and its oxygen neighbors and the Li atoms were fully ionized in the self-consistent

charge density.

These results are consistent with the energetics and electronic structures results, all pointing to the same conclusion that the driving mechanism behind the ferroelectric instability in the $\text{LiNb}(\text{Ta})\text{O}_3$ systems is the hybridization between the d states on the transition metal atoms and the 2p states on the oxygens. The lithiums are but passive players in the ferroelectric instability. This is very similar to the ferroelectric mechanism in the perovskite ferroelectrics, where the oxygen-transition metal atom hybridization, in addition to the Coulombic long range interaction which tend to drive the system off center, overcome the short range repulsions which tend to leave the system in it's high-symmetry configuration.

An interesting comparison can be made with the $\text{K}(\text{Nb},\text{Ta})\text{O}_3$ system; one major difference is the fact that the perovskite KTaO_3 is an incipient ferroelectric where LiTaO_3 has a high transition temperature. In this sense a qualitative comparison can be made between the two sets of systems, as in both systems the transition temperature is higher in the niobate systems, being zero for KTaO_3 . This would mean a shallower well for the tantalates, where in the case of KTaO_3 the well is apparently lower than the thermal vibrations, as shown by this study for the $\text{Li}(\text{Nb},\text{Ta})\text{O}_3$ systems and by Postnikov for the $\text{K}(\text{Nb},\text{Ta})\text{O}_3$ systems²⁹.

The electronic structures of the two sets of systems ($\text{LiNb}(\text{Ta})\text{O}_3$ and $\text{KNb}(\text{Ta})\text{O}_3$) show a large hybridization between the transition metal atoms and the oxygens, and the amount of hybridization between the transition metals and the oxygens in the two sets of systems is similar. This can be seen from Fig. 6b which shows both the partial density of Nb 4d states and that of Ta 5d states in the valence bands in the ferroelectric configuration in the $\text{LiNb}(\text{Ta})\text{O}_3$ systems. We can compare these results to the same densities of states calculated for KNbO_3 and KTaO_3 by LMTO²⁹ reproduced in Fig. 11. These figures show the Nb (Ta) density of states with the Nb (Ta) atom undisplaced and displaced by $0.073a$ (a being the lattice constant) along the $\langle 111 \rangle$ direction, which is an exaggerated displacement used to enhance the differences between the two phases. We can see that the same trends exists in this picture as in Fig. 6b for the Nb (Ta) in LiNbO_3 (LiTaO_3). The ferroelectric peaks at the bottom of this band are slightly shifted towards higher energies. In both cases

there is large hybridization between the transition metal atoms and the oxygens, but this hybridization does not change much during the transition. This hybridization is essential for the onset of the ferroelectric instability, however the amount of hybridization in this system doesn't change much through the phase transition like in other ferroelectrics, e.g BaTiO₃ or PbTiO₃⁵⁴.

We find that LiNbO₃ and LiTaO₃ are almost identical in their electronic behavior. The amount of d character in the valence bands, which is a measure of the hybridization between the transition metal ions and their oxygen neighbors is very similar. This is in contrast to the conclusion that Ta is less ionic than Nb, reached by Postnikov *et al.* for K(Ta,Nb)O₃. This conclusion was based on the smaller transition metal atom density of states peak at the bottom of the valence band, observed in Figures 11a and b. It is seen from Fig. 10 that the origin of this peak is the less dispersive nature of one LiTaO₃ band versus LiNbO₃.

The similarity between LiNb(Ta)O₃ and KNb(Ta)₃ is the fact that the driving mechanism for the phase transition in the two systems is oxygen-B atom hybridization. The difference between the two systems lies in the different structure which yields a different oxygen-A atom interaction.

In both LiNb(Ta)O₃ and KNb(Ta)O₃ the hybridization between the B atoms (the transition metals) and the oxygens causes the oxygens and the B atoms to displace towards each other. In the LiNb(Ta)O₃ system the oxygen-B atom separation is larger than the sum of their ionic radii and the oxygens markedly displace in the a-b plane as they move along the polar axis. This however, makes the oxygen-A atom separation larger than the sum of their ionic radii resulting in the coupled oxygen-A atom motion. This is in contrast to the perovskites where the A site is large enough to allow the oxygens to move towards the A atoms, e.g. KNbO₃ where the potassium-oxygen separation in the highest and lowest symmetry structures are about 2.85 Å and 2.83 Å, respectively, compared with the sum of their ionic radii which is about 2.78 Å.

It is interesting to note that when doping KTaO₃ with lithium atoms (KLT), the system does displace off-center, with a critical concentration of lithiums as small as 2.2%⁶⁸. This

could be the result of the lithium ion having a much smaller ionic radii then the potassium with respect to the perovskite structure, being about 0.6 \AA for Li and 1.4 \AA for K⁵⁹. This would allow the lithiums, driven by Madelung forces, to displace off-center, and due to the large space open to the lithiums in the perovskite structure their amplitudes will be much larger then in the LiTaO₃ system, resulting in a dipole field that polarizes the oxygens and distorts them into off-center positions. The phase transition in KLT is significantly different then in a conventional ferroelectric and there is some discussion of whether KLT is a true ferroelectric. DiAntonio *et al.*⁷⁰ concluded that the coincidence of the temperature of the maximum of the dielectric permittivity with the appearance of other anomalies that are characteristics of a structural transformation are a sign that the transition is ferroelectric, whereas Azzini *et al.*⁶⁹ state that the size of the domains having a homogeneous spontaneous polarization is significantly smaller than the size of the structural domains.

In the Slater picture of the so called “rattling ion”, the B atom lies off center because it is too small to fit into the oxygen octahedra surrounding it. This is in fact the opposite of the picture in the LiNb(Ta)O₃ systems where the separation of the oxygens from the Nb (Ta) atoms are smaller (1.9 \AA) then the sum of their ionic radii (2 \AA). Also, a comparison of the Ta-O distances in KTaO₃ and LiTaO₃ shows exactly this same effect. In KTaO₃, the oxygen octahedra is *larger* than the oxygen octahedra in LiTaO₃, and yet, in KTaO₃ the B atom never displaces to the off center position, while in LiTaO₃, the B cation exhibit a ferroelectric distortion.

IV. CONCLUSIONS

It is shown that LiNbO₃ and LiTaO₃ are very similar in both their electronic structure and energetics. The differences in their well depth are very small, the amount of hybridization in the two materials is similar and the charge densities are similar. Also, these two materials hardly change their electronic structure during a phase transition. The only difference found between these two systems is the difference in the conduction bands. Zone boundary effects

which are not included in this study and this difference in the electronic structure of the two systems are two possible candidates to explain the difference in the transition temperatures of the two systems.

It is demonstrated that contrary to previous models which emphasized the hopping of the lithium atoms between the three positions as the driving mechanism for the phase transformation, in these systems, no triple well potential was found for the lithium motion. The deep double wells found are the result of the oxygen displacements towards the transition metal atoms, which are the result of the hybridization between the two atoms. The wells indicate an order-disorder character for the oxygen. Local changes in the oxygen octahedra are responsible for the lithium displacements from their centrosymmetric sites. The lithiums themselves are passive players in the ferroelectric energetics.

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TABLES

TABLE I. Total Energies for different configurations. a) LiNbO₃. b) LiTaO₃. Coordinates are in primitive rhombohedral coordinates. The first column refers to the displaced atom and the amount of displacement as a fraction of the paraelectric to experimental ferroelectric normal mode amplitude.

a.) LiNbO ₃			
Atomic positions	Li	O	E (Ryd+16193)
Paraelectric	0.25,0.25,0.25	0.136,0.363,-0.25	-0.8462
			-0.8464 ^a
Li - 0.5	0.2645,0.2645,0.2645	0.136,0.363,-0.25	-0.8465
Li - 1.0	0.279,0.279,0.279	0.136,0.363,-0.25	-0.8467
Li - 1.55	0.295,0.295,0.295	0.136,0.363,-0.25	-0.8422
O - 0.75	0.25,0.25,0.25	0.1231,0.3624,-0.2687	-0.8502
O - 1.05	0.25,0.25,0.25	0.1179,0.3621,-0.2761	-0.8498
O - 1.3	0.25,0.25,0.25	0.1135,0.3615,-0.2874	-0.8473
O+Li - 0.5	0.2645,0.2645,0.2645	0.1276,0.3629,-0.2625	-0.8539
O+Li - 0.75	0.272,0.272,0.272	0.1231,0.3624,-0.2687	-0.8586
O+Li - 1.0 ^b	0.279,0.279,0.279	0.1188,0.3622,-0.2749	-0.8638
			-0.8644 ^a
O+Li - 1.05	0.2804,0.2804,0.2804	0.1179,0.3621,-0.2761	-0.8643
O+Li - 1.3	0.288,0.288,0.288	0.1135,0.3618,-0.2834	-0.8639 ^c
O+Li - 1.5	0.294,0.294,0.294	0.1099,0.3615,-0.2874	-0.8579 ^d
b.) LiTaO ₃			
Atomic positions	Li	O	E (Ryd+ 63395)
Paraelectric	0.25,0.25,0.25	0.136,0.363,-0.25	-0.07834
			-0.07830 ^a
Li - 0.5	0.2645, 0.2645,0.2645	0.136,0.363,-0.25	-0.0784

Li - 1.0	0.279,0.279,0.279	0.136,0.363,-0.25	-0.0778
Li - 1.55	0.295,0.295,0.295	0.136,0.363,-0.25	-0.0716
O - 0.75	0.25,0.25,0.25	0.1231,0.3624,-0.2687	-0.0843
O - 1.05	0.25,0.25,0.25	0.1179,0.3621,-0.2761	-0.0806
O - 1.3	0.25,0.25,0.25	0.1135,0.3615,-0.2874	-0.0719
O+Li - 0.5	0.2645,0.2645,0.2645	0.1276,0.3629,-0.2625	-0.0898
O+Li - 0.75	0.272,0.272,0.272	0.1231,0.3624,-0.2687	-0.0939
O+Li - 1.0 ^b	0.279,0.279,0.279	0.1188,0.3622,-0.2749	-0.0957
			-0.0960 ^a
O+Li - 1.05	0.2804,0.2804,0.2804	0.1179,0.3621,-0.2761	-0.0954
O+Li - 1.3	0.288,0.288,0.288	0.1135,0.3618,-0.2834	-0.0914 ^e
O+Li - 1.5	0.294,0.294,0.294	0.1099,0.3615,-0.2874	-0.0809 ^f

^aCalculated using 28 k-points in the irreducible Brillouin zone to test convergence. Other points included 10 k-points.

^bThis is the experimental ferroelectric distortion.

^cEnergy shift due to different muffin tin sizes is included as described in the text. Energy shift is 6.64 mRy.

^dEnergy shift due to different muffin tin sizes is 6.6 mRy.

^eEnergy shift due to different muffin tin sizes is 7.14 mRy.

^fEnergy shift due to different muffin tin sizes is 9.68 mRy.

TABLE II. Bond length, in Å, of transition metals-oxygens and Li-oxygens in different configurations. Sum of ionic radii of each pair is about 2 Å.

a.) LiTaO_3

	Paraelectric	Oxygen Only Distortions Along c axis Only	Oxygen Only Distortions Along soft-mode coordinate	Ferroelectric (Li+O)
Li-O	1.99	2.00	1.96	2.04
Ta-O	1.97	1.86	1.91	1.91

b.) LiNbO_3

	Paraelectric	Oxygen Only Distortions Along c axis Only	Oxygen Only Distortions Along soft-mode coordinate	Ferroelectric (Li+O)
Li-O	1.99	2.01	1.96	2.07
Nb-O	1.97	1.83	1.89	1.89

TABLE III. Parameter table for the polynomial fit of the LAPW and Madelung energies. Energies are in Ryd. LAPW LiNbO₃ energies are shifted by -16193 Ryd and LAPW LiTaO₃ energies by -63395 Ryd.

a.) LiNbO₃

Coefficient	LAPW energies	Madelung energies
Const	-0.8467(3)	-31.7268(0)
Q_{Li}^2	-0.0005(4)	0.0194(0)
Q_O^2	-0.0075(9)	-0.0857(1)
$Q_{Li}Q_O$	-0.0115(8)	0.0040(0)
$Q_{Li}^2Q_O^2$	0.0017(3)	
Q_{Li}^4	0.0003(1)	
Q_O^4	0.0038(5)	
	$R^2 = 0.997$	$R^2 = 0.999$

b.) LiTaO₃

Coefficient	LAPW energies	Madelung energies
Const	-0.0800(11)	-31.7714(0)
Q_{Li}^2	0.0009(14)	0.0200(8)
Q_O^2	-0.0117(30)	-0.0812(13)
$Q_{Li}Q_O$	-0.0121(30)	0.0030(8)
$Q_{Li}^2Q_O^2$	0.0010(11)	
Q_{Li}^4	0.0001(3)	
Q_O^4	0.0090(2)	
	$R^2 = 0.968$	$R^2 = 0.996$

FIGURES

FIG. 1. The a) paraelectric and b) ferroelectric structures of LiTaO_3 and LiNbO_3 . The hexagonal unit cell is outlined.

FIG. 2. a.) Potential energy surfaces of LiTaO_3 . The upper curves represent displacements of the Li atoms along the soft-mode coordinate, the middle shallow double wells represent displacements of the oxygens alone and the bottom curves represent the displacements of oxygens and Li atoms along the same coordinate. The curves represent a 4th order polynomial fit to the data. They were not constrained to go through the zero of energy. The abscissa represents displacement of the oxygen atoms from the paraelectric configuration, in Å. b.) The same for LiNbO_3 .

FIG. 3. The energy as a function of normal coordinate, fitted to a quadratic. The lines are the eigenstates for the 1-D independent harmonic oscillators. The difference between the ground state and the lowest excited state gives a frequency of 270 cm^{-1} for LiTaO_3 and 250 cm^{-1} for LiNbO_3 . Both are in very good agreement with experimental results. a) Energy versus normal coordinate for LiTaO_3 and b) The same for LiNbO_3 .

FIG. 4. Total energy surfaces of LiNbO_3 with only oxygens displaced along soft mode coordinate (lower curve) and with only the oxygens displaced along the c axis only (upper curve). The curves are a 4th order fit to the data. The abscissa represents displacements, in \AA , of the oxygens from their paraelectric positions.

FIG. 5. LiNbO_3 : Charge density resulting from subtracting the charge density of a configuration in which oxygens only are displaced from the charge density of the full ferroelectric distortion (both lithiums and oxygens are displaced). The scale is from -0.1 to 0.1 electrons per bohr^3 and the contour interval is 0.002 electrons/ bohr^3 . No evidence for dynamical covalency effects that would lead to coupling of oxygen and lithium motions are seen

FIG. 6. a) Electronic density of LiTaO_3 (solid line) and LiNbO_3 (dashed line), both in the experimental ferroelectric configuration. b) Density of Ta 5d states (solid line) and Nb 4d states (dashed line) in the valence band, both the experimental ferroelectric configuration. c) Oxygen p states of LiTaO_3 (solid line) and of LiNbO_3 (dashed line) in the valence band, in the ferroelectric phase.

FIG. 7. a) Electronic density of states for LiNbO_3 in the paraelectric (solid line) and ferroelectric (dashed line) configurations. b) The Nb 4d state in the two phases. c) The LiTaO_3 Ta 5d states in the two phases. d) The LiNbO_3 's p states on the oxygens in the paraelectric and the ferroelectric phase. e) The s orbital on the Li atom of LiNbO_3 in the two phases. The valence band top is lined up with the zero of energy.

FIG. 8. The band structure of LiNbO_3 in the ferroelectric phase. The energy scale is in eV and the fermi level is shown. The band gap is 3.1 eV. The Li s states do not interact with the rest of the bands and are about 16 eV below the Oxygen 2s states. Inset: The brillouin zone. Some high symmetry points are illustrated. The energy between the Z and the A point was calculated along a straight line between the two points. From [60].

FIG. 9. a) The band structure of LiTaO_3 in the ferroelectric phase (solid line) and the paraelectric (dashed line). Only the valence and the conduction bands are shown. The band gap in the ferroelectric phase is about 4.0 eV, and is decreased in the paraelectric phase by about 15 %. b) The same for LiNbO_3 . The gap decreases by about 15 % between the ferroelectric and paraelectric phases. No major differences are observed in both systems between the two phases.

FIG. 10. The band structure of LiNbO_3 (solid line) and LiTaO_3 (dashed line), both in the ferroelectric structure. The LiTaO_3 band gap is larger than the LiNbO_3 band gap by about 1 eV. The valence bands of the two materials are almost identical.

FIG. 11. From LMTO results of KTaO_3 and KNbO_3 , by Postnikov *et al.* [29]. a) Local densities of states at the Nb site with the Nb undisplaced (solid line) and displaced (dashed line) from its rhombohedral position. The displacement of the Nb atom is exaggerated in order to enhance the trends shown. b) at the Ta site, under the same conditions. The units are in Ryd for the energies and Ryd^{-1} for the density of states.

























